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COMPLETE SPECIFICATION

Improvements in or relating to the manufacture of Luminescent Materials

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Glen House, Star Place, Victoria, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of luminescent materials, one object of the invention being to provide a method of manufacturing luminescent materials of novel composition which are excited to luminescence by one or more of the usual exciting agencies, namely ultra violet radiation of long wavelength (that is to say of wavelength greater than 3000 Å), ultra violet radiation of short wavelength (that is to say of wavelength less than 3000 Å), cathode rays, and X-rays.

The invention also includes within its scope luminescent materials manufactured by the method described and electrical devices, such as high and low pressure mercury vapour fluorescent electric discharge lamps, cathode ray tubes, and X-ray screens, which incorporate one or more luminescent materials manufactured in accordance with the invention, arranged so as to be excited to luminescence during the operation of the device.

According to the present invention, a method of manufacturing a luminescent material comprises heating a starting material consisting of or containing the elements magnesium, lithium, antimony, fluorine, silicon and/or germanium, oxygen, and manganese, the relative proportions of said elements present and the temperature at which and length of time for which said starting material is heated being such that there is formed a reaction product consisting only of the elements magnesium, lithium, antimony, fluorine, silicon and/or germanium, oxygen, and manganese, being composed essentially of, in combi-

nation, the oxides of magnesium, lithium, antimony, and silicon and/or germanium, and lithium fluoride, and activated by manganese in the tetravalent state so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å.

In a modification of the invention, the starting material also contains one or more divalent metals of Group II of the Periodic Table of the elements, in addition to magnesium, preferably one or more of the alkaline earth metals calcium, strontium, and barium. Such additional metal is preferably introduced into the starting material in the form of a fluoride of the metal, which may wholly or partly replace the lithium fluoride in the reaction product obtained.

The starting material may conveniently consist of an intimate mixture of magnesium oxide, an antimony oxide, silicon dioxide or germanium dioxide or both silicon and germanium dioxides, lithium carbonate, lithium fluoride and/or one or more fluorides of additional divalent metals as aforesaid, and a suitable compound of manganese: one or more of the oxides in the said mixture may be replaced by a compound which decomposes on heating to give the oxide, such as a carbonate. The manganese may be introduced in the form of an aqueous solution of a water-soluble salt from which, on heating, the manganese can be incorporated in the reaction product in the tetravalent state. The mixture is dried, ground to a powder, and fired in air at temperatures in the range of 900° C. to 1200° C.: preferably the mixture is subjected to two or more firing steps at successively higher temperatures, the material being reground after each firing step.

The relative proportions of the elements in the starting material may be varied over a wide range, but we have found that reaction

products having particularly useful luminescent properties are obtained from starting materials of compositions such that the relative molecular proportions of magnesium oxide (MgO), lithium oxide (Li₂O), lithium fluoride (LiF), antimony trioxide (Sb₂O₃), and silicon dioxide (SiO₂) and/or germanium dioxide (GeO₂) derived therefrom lie within the following ranges:—

MgO:Li₂O in the range of 4.4:0.1 to 1.0:3.5,

Li₂O:LiF in the range of 0.5:1.5 to 1.9:0.1,

Sb₂O₃:SiO₂+GeO₂ in the range of 0.05:0.95 to 0.5:0.5, the preferred ratio being 0.25:0.75.

The total molecular proportions of (MgO+Li₂O+LiF) may suitably be from four to six times the total molecular proportions of (Sb₂O₃+SiO₂+GeO₂), a preferred ratio of (MgO+Li₂O+LiF):(Sb₂O₃+SiO₂+GeO₂) being 4.75:1. The lithium fluoride may, if desired, be replaced by one or more fluorides of divalent metals, especially the alkaline earth metals, as indicated above: in this case, the molecular proportion of divalent metal fluoride may be somewhat smaller than that of the lithium fluoride replaced: for example, 1.0 mole of LiF may be replaced by 0.25 mole of calcium fluoride, CaF₂, a preferred ratio of (MgO+Li₂O+CaF₂):(Sb₂O₃+SiO₂+GeO₂) being 4:1. (It will be understood that in the molecular ratios given above, where "SiO₂+GeO₂" is referred to, either SiO₂ or GeO₂ may, if desired, be zero).

The proportion of manganese incorporated as an activator in accordance with the invention is preferably in the range of 0.001% to 0.5% by weight of the reaction product, the optimum brightness of luminescence usually being obtained with a manganese content of about 0.05% by weight.

The chemical constitution of the luminescent materials manufactured by the method of the invention has not yet been fully ascertained, but it is believed that the materials

may be complex fluosilicates or fluogermanates or fluosilico-germanates of magnesium, lithium and antimony, with or without one or more additional divalent metals as aforesaid, with tetravalent manganese incorporated in the fluosilicate, or fluogermanate, or fluosilico-germanate, crystal lattice as an activator. It is possible that a part of the antimony present may be incorporated in the lattice in such a manner that it also functions as an activator. X-ray powder photographs show the materials to have a crystal structure of some complexity: the form of the diffraction pattern, however, indicates that the structure is derived from that of magnesium oxide, and is probably an ordered arrangement incorporating lithium and silicon/germanium atoms with magnesium atoms in a nearly cubic packed oxygen network.

The luminescent materials manufactured by the method of the invention are excited by ultra violet radiation of both short wavelength (for example 2537 Å) and long wavelength (for example 3650 Å) to exhibit luminescence of a red or pink colour, the emission spectrum lying mainly between 6500 Å and 6800 Å. These phosphors are thus suitable for use in both high and low pressure mercury vapor fluorescent electric discharge lamps. In general the luminescence produced under excitation by long wavelength U.V. is brighter than that obtained under excitation by short wavelength U.V.

It will be understood that the ingredients of the starting materials employed in the method of the invention should be of a high degree of purity, as is usual in the manufacture of luminescent materials.

Some specific methods, in accordance with the invention, which we have employed for the manufacture of luminescent materials, will now be described in the following examples.

EXAMPLE 1

For the production of a material having a composition which may be regarded as a magnesium calcium lithium antimony fluosilicate, activated by manganese, an intimate mixture of the following ingredients was prepared:—

	Magnesium oxide (MgO)	44.5 grams
	Calcium fluoride (CaF ₂)	6.3 grams
95	Lithium carbonate (Li ₂ CO ₃)	24.0 grams
	Silica (SiO ₂) (allowing for 13.3% water content)	16.6 grams
	Antimony trioxide (Sb ₂ O ₃)	23.7 grams

These dry ingredients were thoroughly mixed with 50 mls. of a 0.1% (weight/volume) solution of manganese chloride in

water, and the mixture was dried at a temperature of 130° C.

The dried mixture was ground to a fine

powder, which was placed in a silica tray and fired at 1000° C. for one hour in air. The fired material was again ground, fired at 1050° C., reground, and finally fired at 1100° C., all the firing steps taking place in air. It was found that some sintering had taken place during the final firing.

The powder obtained on grinding the material after the final firing had a pinky-beige body colour, and showed a red fluorescence when excited by ultra violet radiation of wavelength 3650 Å, and a weak pink fluorescence when excited by ultra violet radiation of wavelength 2537 Å. The emission spectrum showed a narrow band type of structure, characteristic of tetravalent manganese.

The quantities of the ingredients forming the starting material would, on firing, give a reaction product having substantially the molecular composition indicated by the formula 3.5 MgO:0.25 CaF₂:1 Li₂O:0.75 SiO₂:0.25 Sb₂O₃, with 0.05% by weight of manganese.

EXAMPLE 2

A material which can be regarded as a magnesium lithium antimony fluosilicate having substantially the molecular composition represented by the formula 3.5 MgO:1 Li₂O:1 LiF:0.75 SiO₂:0.25 Sb₂O₃, activated by 0.05% by weight of manganese, was prepared from a mixture of the following ingredients:

Magnesium oxide (MgO)	44.6 grams
Lithium carbonate (Li ₂ CO ₃)	23.6 grams
Lithium fluoride (LiF)	8.3 grams
Silica (SiO ₂) (allowing for 13.3% water content)	16.2 grams
Antimony trioxide (Sb ₂ O ₃)	23.2 grams
Manganese chloride (0.1% aqueous MnCl ₂ solution)	
	50 mls.

This mixture was dried at 130° C. and ground to powder, which was fired in air in an open silica tray: the firing was carried out in two stages, the first at 1000° C. and the second at 1100° C., each for one hour, the material being ground after each firing: some sintering had again occurred in the final firing.

The final product was a powder of a pale orange body colour. This powder showed a red fluorescence under 3650 Å ultra violet

radiation, and a weak pink fluorescence under 2537 Å ultra violet radiation.

EXAMPLE 3

For the preparation of a material having a composition corresponding to the formula 2.75 MgO:1 Li₂O:0.25 CaF₂:0.75 SiO₂:0.25 Sb₂O₃, activated by 0.05% manganese, a starting mixture consisting of the following ingredients was prepared:—

Magnesium oxide (MgO)	39.8 grams
Calcium fluoride (CaF ₂)	7.0 grams
Lithium carbonate (Li ₂ CO ₃)	26.6 grams
Silica (SiO ₂) (allowing for 13.3% water content)	18.4 grams
Antimony trioxide (Sb ₂ O ₃)	26.2 grams
Manganese chloride (0.1% aqueous MnCl ₂ solution)	
	50 mls.

These ingredients were mixed to paste with additional water, and the mixture was dried at 130° C. and ground to a powder. The powder

was fired in air in an open silica tray, in three stages, at 1000° C. for one hour, at 1050° C. for one hour, and at 1075° C. for one hour, the

material being ground after each firing step: the product of the final firing was a hard sintered mass.

5 The powder obtained after grinding the sintered material had a pale orange body colour, and emitted a red fluorescence when excited by 3650 Å radiation and a weak pink fluorescence when excited by 2537 Å radiation.

10 The luminescent materials manufactured in accordance with the invention possess moderately good temperature stability. For example, the materials produced by the methods de-

scribed in the above specific examples continue to emit some red fluorescence at temperatures exceeding 250° C.

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EXAMPLE 4

In the method of this Example, a material having a composition which may be regarded as a magnesium calcium lithium antimony fluogermanate, activated by tetravalent man- 20 ganese, was prepared from a starting material consisting of an intimate mixture of the following ingredients:—

Magnesium oxide	(MgO)	34.7 grams
Calcium fluoride	(CaF ₂)	6.15 grams
Lithium carbonate	(Li ₂ CO ₃)	23.4 grams
Germanium oxide	(GeO ₂)	26.5 grams
Antimony trioxide	(Sb ₂ O ₃)	23.0 grams

25 These dry ingredients were thoroughly mixed with 50 mls. of a 0.1% (weight/volume) solution of manganese chloride in water, and the mixture was dried at 130° C.

30 The dried mixture was ground to a fine powder, which was placed in a silica tray and fired at 1000° C. for one hour in air. The fired material was again ground, fired at 1100° C. in air, reground, and finally fired at 1150° C. in air. It was found that some sintering 35 had taken place during the final firing.

The powder obtained on grinding the material after the final firing step had a pinky-orange body colour. The powder showed a red fluorescence when excited by ultra violet radiation of wavelength 3650 Å, and a weak pink fluorescence when excited by ultra violet radiation of wavelength 2537 Å.

40 The quantities of the ingredients forming the starting material would, on firing, give a reaction product having substantially the molecular composition indicated by the formula 2.75 MgO:0.25 CaF₂:1 Li₂O:0.75 GeO₂:0.25 Sb₂O₃ with 0.05% by weight of manganese.

50 This material possesses moderately good temperature stability, since it continues to emit fluorescence at temperatures up to about 250° C.

WHAT WE CLAIM IS:—

55 1. A method of manufacturing a luminescent material which comprises heating a starting material consisting of or containing the elements magnesium, lithium, antimony, fluorine, silicon, and/or germanium, oxygen, and manganese, the relative proportions of said 60 elements present and the temperature at which and length of time for which said starting material is heated being such that there is formed a reaction product consisting only of

the elements magnesium, lithium, antimony, 65 fluorine, silicon and/or germanium, oxygen, and manganese, being composed essentially of, in combination, the oxides of magnesium, lithium, antimony, and silicon and/or germanium, and lithium fluoride, and activated by man- 70 ganese in the tetravalent state so as to be excitable to luminescence by ultra violet radiation of wavelength 2537 Å and of wavelength 3650 Å.

2. A method according to Claim 1, with the 75 modification that the starting material also contains one or more divalent metals of Group II of the Periodic Table of the elements, in addition to magnesium, which additional metal is introduced into the starting material in the 80 form of a fluoride, which may wholly or partly replace the lithium fluoride in the reaction product obtained.

3. A method according to Claim 2, wherein 85 the said additional divalent metal or metals is or are one or more of the alkaline earth metals calcium, strontium, barium.

4. A method according to Claim 1, 2 or 3, 90 wherein the starting material consists of an intimate mixture of magnesium oxide, an antimony oxide, silicon dioxide or germanium dioxide or both silicon and germanium dioxides, lithium carbonate, lithium fluoride and/or one or more fluorides of said additional divalent 95 metals, and a suitable compound of manganese, one or more of said said oxides optionally being replaced by a compound which decomposes on heating to give the oxide.

5. A method according to Claim 4, wherein 100 the manganese is introduced into the starting material in the form of an aqueous solution of a water-soluble salt from which, on heating, the manganese can be incorporated in the reaction product in the tetravalent state, and

wherein the starting mixture is dried, ground to a powder, and fired in air at temperatures in the range of 900° C. to 1200° C.

6. A method according to Claim 5, wherein the said mixture is subjected to two or more firing steps at successively higher temperatures, the material being reground after each firing step.
7. A method according to any preceding Claim, wherein the composition of the starting material is such that the relative molecular proportions of magnesium oxide (MgO), lithium oxide (Li₂O), lithium fluoride (LiF), antimony trioxide (Sb₂O₃), and silicon dioxide (SiO₂) and/or germanium dioxide (GeO₂) derived therefrom lie within the following ranges:—
 - MgO:Li₂O in the range of 4.4:0.1 to 1.0:3.5.
 - Li₂O:LiF in the range of 0.5:1.5 to 1.9:0.1.
 - Sb₂O₃:(SiO₂+GeO₂) in the range of 0.05:0.95
 and the total molecular proportions of (MgO+Li₂O+LiF) are from four to six times the total molecular proportions of (Sb₂O₃+SiO₂+GeO₂).
8. A method according to Claim 7, wherein the composition of the starting material is such that the ratio of Sb₂O₃:(SiO₂+GeO₂) derived therefrom is 0.25:0.75.
9. A method according to Claim 7 or 8, wherein the composition of the starting material is such that the ratio of (MgO+Li₂O+LiF):(Sb₂O₃+SiO₂+GeO₂) derived therefrom is 4.75:1.
10. A method according to Claim 7, 8, or 9, with the modification that the lithium fluoride is replaced by a smaller molecular proportion of one or more divalent metal fluorides, in accordance with Claim 2 or 3.

11. A method according to Claim 10, wherein the lithium fluoride is replaced by calcium fluoride, 1.0 mole of lithium fluoride being replaced by 0.25 mole of calcium fluoride.

12. A method according to any preceding Claim, wherein the proportion of manganese incorporated in the luminescent material as an activator is in the range of 0.001% to 0.5% by weight of the reaction product.

13. A method according to Claim 12, wherein the proportion of manganese incorporated in the luminescent material as an activator is 0.05% by weight of the reaction product.

14. A method of manufacturing a luminescent material, carried out substantially as hereinbefore described in any one of the specific Examples 1 to 4.

15. A luminescent material manufactured by a method according to any preceding Claim.

16. An electrical device in which is incorporated a luminescent material according to Claim 15, said material being arranged so as to be excited to luminescence during the operation of the device.

17. A high pressure mercury vapour fluorescent electric discharge lamp which includes a luminescent material according to Claim 15, said material being arranged so as to be excited to luminescence by the electric discharge passing through the lamp.

18. A low pressure mercury vapour fluorescent electric discharge lamp which includes a luminescent material according to Claim 15, said material being arranged so as to be excited to luminescence by the electric discharge passing through the lamp.

For the Applicants,
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